preferentially adsorb one layer MW

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EXPERIMENTAL STATION
CHEMICALS, DYES & PIGMENTS DEPARTMENT
RESEARCH & DEVELOPMENT DIVISION
E. I. DU PONT DE NEMOURS & CO., INC.

TiO_2 PIGMENTS FOR INDUSTRIAL APPLICATIONS

POLYESTER WATERBORNE SYSTEMS

PROGRESS REPORT

Work Done By:	L. J. Matienzo
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ABSTRACT

A systematic study of the different steps involved in the formation of the dry film of a water-reducible polyester will allow to determine the factors controlling the deficient hiding of R-900 in this formulation.

Techniques to study adsorption of acrylic and polyester water-reducible resins on Ti-Pure® surfaces have been developed and conclusions on the nature of the initial adsorption process have been drawn.

N40788

R. J. Bouchard 9/23/80
R. J. Bouchard Date

INTRODUCTION

Business Objective:

Develop understanding of technical requirements for and behavior of TiO_2 in new industrial systems (waterborne, high solids, radiation cured, etc.). Develop pigment to meet specific needs as they are identified (e.g., high hiding TiO_2 in water-reducible polyesters).

Incentive:

To ensure Ti-Pure® performance in new systems. Projections are:

	% of Industrial Market		
System	1977	(1982)	1987
Solvent-borne	91		30
Waterborne	5	20	35
High-solids	1	10	20
Powder	3		5
Others	-		10
	100		100

TiO_2 use in industrial coatings has been projected to be 210 MT in 1982 corresponding to ~30MT/Y Ti-Pure® sales to water-borne and high-solids systems.

OBJECTIVES

A grade of pigment with high gloss and comparable hiding to that developed in an acrylic waterborne system (American Cyanamid XC-4011) is not available from any manufacturer for industrial polyester systems.

The design and selection of such a pigment or a dispersant needed to produce this improvement requires an understanding of surface, dispersant and vehicle interactions in the solvent medium. Fundamental studies in this area of waterborne polyesters are scant, therefore, experimental methods to develop useful information have been investigated.

SUMMARY AND CONCLUSIONS

Polyester and Acrylic Waterborne Systems

- Defined system to study adsorption of vehicles onto Ti-Pure® pigments from aqueous solutions.

- Developed size exclusion chromatography to detect adsorption of polyester from solution.

- Demonstrated that preferential adsorption of higher molecular weight fractions occurs under similar conditions to those existing in finished paints.

- Improved size exclusion chromatography to provide quantitative data on polymer adsorption. Developed first Langmuir adsorption isotherm of this type.

- Showed that polyester adsorption on R-900 is a very fast process and the pigment behaves like alumina.

- Developed reverse phase liquid chromatography to detect adsorption of molecules from solution and allow direct sampling of slurries.

- Since a liquid chromatograph was not available in the laboratory, developed a faster technique to detect adsorption using ultraviolet spectroscopy.

- Showed agreement between data obtained by liquid chromatography and new technique.

- Determined equilibrium time required for reaction of R-900 (28), R-960 (01), dense silica coated pigment (3% SiO_2) and clean R-900 base with both acrylic and polyester waterborne vehicles.

- Obtained adsorption isotherms for R-900 (28), R-960 (01) and R-931 (01) pigments with both acrylic and polyester vehicles.

- Showed that R-900 C.D. material (Line I, New Johnsonville) behaves like finished product toward adsorption of polyester from solution: alumina is concentrated on base surface.

PATENT STATUS

No patent action is contemplated.

PROGRAM

This program has been dropped.

PUBLICATION STATUS

There are no plans to publish this work at the present time.

SPECIAL SAFETY PRECAUTION

The only consideration is to have enough ventilation when resins and paints are handled.

ENVIRONMENTAL CONSIDERATIONS

None.

CHEMICALS USED

R-900 (28), R-960 (01), R-931 (01), Rutile 99.99% TiO_2 (SPEX Ind.), Cyplex 1600 polyester solution, American Cyanamid acrylic solution XC-4011, Tetrahydrofuran, Dimethylethanolamine (DMEA), Toluene and Methanol.

TOXICITY DATA

None.

SPECIAL PRECAUTIONS

None.

ASSISTED BY

L. J. Janvier.

ACKNOWLEDGEMENT

My special thanks to R. E. Johnson, L. Abrams and J. H. Boughton for their interest in this program.

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EXPERIMENTAL AND DISCUSSION

The ultimate result on performance of any type of pigments in a paint formulation is a sum of processes that occur since the moment in which the components of the mill base come into contact with each other. In order to develop an acceptable level of hiding and gloss, pigments have to be dispersed in a vehicle until their particle sizes reach the submicron level. The mean diameter of a TiO_2 primary particle is about 0.2 μm but this smallness ensures aggregation since Van Der Waals forces become important. These short-range forces operate in dispersions of solids in liquids and after the dispersion process stops, the particles may tend to re-aggregate unless a stabilizing mechanism can oppose the forces of attraction.

Two stabilizing mechanisms are known and were described in some detail in my previous report (PTD-SA-78-28). Whatever the stabilization mechanism, a dispersion of pigment particles in a liquid is an equilibrium system, if this state is altered at any stage of the paint manufacture and final application, the end result will show some deficiency performance.

The adsorption of macromolecules plays an important role on dispersion of pigment particles in paints. In order to understand the importance of these interactions in a real system, a simplified model of a waterborne paint must be adopted. Since the amount of material adsorbed by the substrate can only be measured indirectly, i.e., by difference in concentration, one must work with dilute solutions. Then, the type of information that can be derived will answer questions concerning the manner, the energetics and the kinetics of macromolecular attachment, the density of adsorption, the nature of any exchange reactions with solvents or surfactants, and the dependence of these features on the structures of surface, solution and macromolecules. Also, the dependence on such variables like concentration, temperature, pH, zeta potential, electrolytes and cosolutes can be established. Then, one can tie up pigment performance to the type of surface modification required to optimize optical properties in a particular system, in this case polyester waterborne formulations for industrial applications.

Polyester and Acrylic Waterborne Resins

Acrylic and polyester waterborne paints show different behavior associated with the type of pigment, i.e. surface treatment, used. For example, polyester paints containing R-900 have a hiding power which is about 70% of their value in acrylic resins formulated at the same PVC (ca. 21%). The differences in end-results might be related to the adsorption mechanism of polyester and the type of stabilization which controls flocculation.

The materials used for this study were two commercial resins. An acrylic, XC-4011, was chosen as a comparison since previous work on this area had used it extensively. Cyplex 1600, a water soluble polyester, was used for adsorption studies. In general, most commercial polyester resins have similar compositions and analogous behavior in this system.

Since the structure and composition of the vehicles are important to interpret results, concerning the bonding and nature of the adsorbed layer, the physical and chemical characterization of these materials was attempted. Table LJM-I shows the results obtained for the chosen polyester and acrylic. The main features of these are:

- Broad molecular weight distribution
- Different number of carboxylic groups/molecule
- Completely different chemical structure and molecular size.

Once the approximate dimensions of the average molecule are known and the manner in which it attaches itself to the pigment surface, the thickness of the adsorption layer may be estimated.

Experimental Slurry Composition

Since the standard paint formulation with Cyplex 1600 contains about eight to ten components, a simplified model system was chosen for study. The components which comprise about 90% of the mixture were selected, these were:

- Pigment
- Cyplex 1600 or Acrylic XC-4011 resin
- Dimethylethanolamine (DMEA)
- De-ionized water.

Aqueous solutions of resin were made by taking a known amount in a volumetric flask, adding de-ionized water and slowly titrating with DMEA until total dissolution of the resin was detected. The final pH of this solution was adjusted to 8.5-8.6. The slurry samples contained constant limiting ratio of pigment to solution. The slurry concentration was 10.0% PVC, based on R-900.

High Performance Liquid Chromatography Analysis (HPLC)

Liquid chromatography was considered as the initial experimental technique to give information on adsorption from solution. Since polyesters and acrylics have a broad molecular weight distribution, all of the molecules do not have the same

bonding ability toward the pigment surface. A special form of HPLC, was chosen for the determination of selective adsorption. Size Exclusion Chromatography (SEC), based on molecular size separation was chosen for this work. The method of SEC have been described in my previous report (PTD-SA-78-2B). Basic principles would indicate that in the case of macromolecular electrolytes, the larger size molecules will adsorb more easily on a solid surface. Of course both materials, polyesters and acrylics, have different bonding groups. The main adsorption for polyester occurs through ester linkages which hydrogen-bond onto the hydroxylated surface. An average of three ester groups and a carboxylic group exists in the average size molecule. In contrast, XC-4011 interacts with the pigment mostly through carboxylate linkages.

In a typical experiment, 20.6g of pigment, were placed in a four-ounce jar and 45.0 ml of a solution of known concentration were added. The capped sample was shaken in a Fisher-Kendall® mixer for a known length of time. Then the supernatant solution was gradually separated from the solid by centrifugation. An aliquot of the supernatant was evaporated to dryness and the residue was dissolved in THF and then analyzed using a SEC system. Figure LJM-I shows the type of curves obtained from these experiments. In conclusion, as expected, larger size molecules adsorb preferentially on TiO_2 pigment and flocculation cannot be caused by collapse due to low molecular weight materials adsorbed on the coating.

Quantification of adsorption results are necessary in order to derive an adsorption isotherm. Preliminary tests showed that area integration of the distributions is directly proportional to concentration and this approach was adopted for quantitative analysis. Then, the amount of material adsorbed by the surface can be measured by area differences of the polyester or acrylic solution before and after contact. Figure LJM-II presents the changes on molecular size distribution before, at and after a monolayer coverage of polyester on R-900 as measured by SEC on several samples after contact of solution and pigment. Table II gives the results obtained for Cyplex 1600 and R-900 used to determine the Langmuir adsorption isotherm for the process at room temperature. The method above described has a drawback since samples have to be evaporated to dryness and then carefully diluted with THF before analysis. As an improvement, another HPLC method was designed to allow direct handling of aqueous samples. The technique adopted was Reverse Phase Liquid Chromatography which allows to program solvent polarity and thus separation of molecules at different and controllable rates. Figure LJM-III shows the marked difference after adsorption, although, it is necessary to note that in this case the smaller and more polar molecules elute out of the column first.

The above results conclude that, as predicted, lower molecular weight species remain in solution and in equilibrium with higher size macromolecules adsorbed on the pigment surface. Intermolecular rearrangements, at least with an alumina-only surface, do not occur. Intramolecular re-distributions are expected to continue for some time as detected in organic solvent systems containing simple polyesters (K. Hamman and G. Joppien, 1977). It is expected that after a few hours, about 40 to 70% of the ester-hydroxyl linkages remain undisturbed. About two out of three ester groups remain in contact with the surface and the thickness of the adsorbed layer increases slightly but does not provide enough of a distance to produce steric stabilization. Electrostatic effects then become important at the operating pH, since the macromolecules are ionized.

Ultraviolet Analysis of Polyesters and Acrylics From Aqueous Solutions

As explained above, the adsorption process can be followed by HPLC but sample preparation is rather involved and data handling consumes a relatively large portion of time.

Since aromatic acids or anhydrides are used in the synthesis of commercial polyesters, they absorb strongly in the ultraviolet region of the electromagnetic spectrum. Infrared work has shown that even the nonadsorbing fractions contain these aromatic groups and polyester molecules of all sizes adsorb in the UV. Figure LJM-IV shows the spectrum of a methanolic solution of polyester after contact with R-900. The methanol vs. methanol reference spectrum is added for comparison. The peaks appearing at λ 279 and 288 nm are assigned to $n \rightarrow \pi^*$ transitions. These maxima do not shift on adsorption and their absorbance readings can be used to determine concentrations in the range in which the Beer-Lambert Law is obeyed. Likewise, acrylic resins containing unsaturated bonds which show appreciable UV absorption below 270 nm. Methanolic solutions of XC-4011 have a UV band at 268 nm and this maximum can be used to follow concentration changes. In both cases, methanol solutions are used since this solvent allows the uncoiling of the macromolecules present in aqueous solutions which if not considered, will induce scattering losses in the measurements.

If the concentration range is kept below micelle formation, good linear correlations are possible for both materials. Figure LJM-V prevents typical calibration curves.

A Comparison of Adsorption of Polyester by SEC and UV Methods

Some samples of Cyplex 1600 and R-900 were prepared and the concentration of adsorbed polyester was measured by peak area integration (SEC) or by direct determination of resin in the supernatant solution (UV). The adsorption isotherms for both sets of data are shown in Figure LJM-VI and show that:

- The saturation point or monolayer coverage for Cyplex 1600 on R-900 (28) is 52.5 mg/g by SEC and 49.1 mg/g by UV analysis. 8.38 μmoles/g
- The differences on the above results, although small, are attributed to:
  - Inherent experimental error obtained by any method based on the measurement of concentration differences.
  - Size exclusion chromatography use tetrahydrofuran as the carrier solvent while UV analysis used absolute methanol.
  - The detection by SEC is made at 254 nm while the second technique uses the peak maximum at 288 nm.

In summary, UV spectrophotometric analysis for commercial polyester and acrylic vehicles yields adsorption data as good as any obtained using a more elaborate analytical technique.

Interaction of Polyester and Acrylic on Several Oxide Surfaces

The control on adsorption is governed by the nature of the outermost layer of the pigment present at the solid-liquid interface, and, it is possible to anticipate different behavior as the composition of the coating changes. Ultimately, this will contribute to the performance of the pigment in a waterborne paint composition. Several commercial and experimental pigments were selected to study these effects. The composition of the surface was varied from silica only through silica-alumina mixtures and finally alumina-only coatings. Two types of experiments were performed and these are discussed below.

Kinetic Runs

Since the intention of the present study was to compare macromolecular adsorption with pigment surface composition, the equilibrium time for the process was measured in each case. A sample of polyester or acrylic of known concentration was contacted with pigment and the decay of absorbance of the supernatant

solution was followed as a function of time. The concentration of the solutions was carefully chosen to maintain sub-monolayer coverage. In other words, preliminary runs were made to determine the concentration range in which the pigment surface remained active and showed absorbance changes. Figures LJM-VII and VIII present the curves obtained with four different pigments in polyester and acrylic solutions respectively. Table LJM-III summarizes the equilibrium times for both sets of experiments. Conclusions:

- An alumina-only surface reaches equilibrium faster than any other pigment.
- More macromolecular adsorption is achieved with an alumina coating.
- The adsorption of polyester and acrylic is minimal for dense silica coated pigments within 100 hours of contact.

Adsorption Isotherms

The adsorption isotherm for any system under investigation was derived by measuring the change in concentration in the liquid phase after equilibrium was attained. In each study, the amount of pigment and the volume of solution were kept constant. The concentration of polyester or acrylic varied gradually from sample to sample and, normally, ten samples were used for each isotherm. Also a calibration curve at the specified wavelength was obtained for the initial solutions and used to measure the unknown concentrations. The isolation of the supernatant solution follows the procedure described in my previous report (PTD-SA-78-2B). The experimental results for R-900 (28), R-931 (01) and R-960 (01) in polyester and acrylic solutions are listed in Tables LJM-IV-IX. Figures LJM-IX and X show the adsorption isotherms for these pigments in both vehicles. The following observations are noted:

- The adsorption process is relatively fast for polyester solutions.
- In both cases, stronger interaction is obtained with an alumina-only surface.
- The approximate monolayer coverages for the pigments are:

Pigment	Cyplex 1600	XC-4011
R-900(28)	45 mg/g	13 mg/g
R-931(01)	40	10
R-960(01)	22	3

- Monolayer coverage for polyester extends to a relatively high concentration range (60-70 g/l) of the supernatant solution.

- Multilayer buildup is noticed above 30 g/l for supernatant solutions containing acrylic resin.

Adsorption on R-900 CD Base Material

In order to determine the adsorption differences between the base and the finished material, a representative sample of R-900 CD (New Johnsonville, Line I) was cleaned according to the procedure developed by L. Abrams (PTD-SA-78-2B, p. 16). The base material usually contains less than 1% co-oxidized alumina. It was hoped that the systematic leaching of the base would produce more of a rutile surface to observe its behavior.

The experimental results showed that:

- Equilibrium with CD material is reached in less than an hour in polyester solutions and the amount adsorbed is comparable to that of R-900.

- The adsorption isotherm for the CD base/polyester material is very close to that of R-900 (28) and actually both sets of data can be plotted on a common isotherm as shown in Figure LJM-XI.

- If the monolayer coverages of R-900 (28) are expressed as equivalents of carboxylic group/gram of pigment, they become: 39×10^{-6} (for Cyplex 1600) and 19×10^{-6} (for XC-4011) equivalents/gram. The monolayer coverages agree well with adsorption concentrations of simple ions on clean R-900 base. For example, the measured concentration of F^- ion on R-900 base is between 20-40 equivalents $\times 10^{-6}$/g. Although we are dealing in our investigation with polyelectrolytes, the adsorption sizes are those available to simple ions.

can't confirm this

what about surface area diff. for R-900 & R-900CD would suggest /m² R-900CD actually adsorbed more.

These observations lead to a reasonable hypothesis: the alumina in the base pigment is highly concentrated on the surface and controls its adsorption behavior.

Adsorption on Pure Titanium Dioxide

To test the hypothesis above described, TiO_2 of 99.99% purity was obtained from SPEX Industries. The analytical characterization of this material is given in Table LJM-X.

Kinetic runs on this material with both polyester and acrylic reveal that no adsorption is observed within 100 hours of contact. One can imagine that if surface contamination by silica occurred, the results could be explained rather easily. For example, if during the synthesis of the titanium dioxide, there is some SiO_2 diffusion to the surface the zeta potential of the solid would tend to approximate that of pure silica. The isoelectric point of pure SiO_2 is below pH 2.0. The sample under investigation has an isoelectric point of about 3.6 to 3.8 pH units. The nonadsorption results may be explained solely on zeta potential values in the neighborhood of the operating pH. For example, at pH 6.4, the particles have a charge of -58 mV and repulsion between polyelectrolyte and pigment will increase.

The possible contamination of silica on the rutile surface can be elucidated by Secondary Ion Mass Spectroscopy (SIMS). Figure LJM-XII is a typical spectrum of the composition of the first monolayers of the rutile sample. The peaks that appear around m/e 47.00 belong to the titanium isotopes and those around m/e 65.00, to their corresponding $TiOH^+$ counterparts. The peak around m/e 28.0 corresponds to silicon. Figure LJM-XIII is an expansion of the region between m/e 22.0 and 33.0. Note the presence of two silicon isotopes in the region of m/e 28.0-29.0

The etching profile of the rutile surface is presented in Figure LJM-XIV and it is clear that there is not that much SiO_2 present.

In view of these results, I can safely conclude that:

- The amount of co-oxidized alumina on the base is enough to provide comparable behavior to a fully coated pigment such as R-900.
- Careful control during alumina deposition may provide equal performance to R-900 for pigments containing less than 3% Al_2O_3.

A Retrospective View on Pigment Surface Chemistry

A combination of analytical techniques and physical measurements enables us to produce a new approach to the understanding of pigment behavior in new industrial systems. The end-point performance is the sum of many complex processes in which adsorption, competition reactions and electrokinetic properties play an interlocking role. The solution of current deficiencies, unusual pigment behavior in well known systems and dispersion behavior must be achieved only by a systematic approach and the understanding of fundamental principles.

TABLE LJM-I

Characterization of Resins

MW KOH = 56.11

XC-4011 Acrylic

Acid Number = 96 — mg KOH/g resin
1.71 mmoles/g

% Solids = 78

Molecular Weight: $\bar{M}n$ = 6060 165 μmoles/g

$\bar{M}w$ = 20800 48 μmoles/g

Composition (molar percent): $\frac{1710}{165}$ = 10 acid groups/mole

Styrene/butylacrylate/hydroxyethylacrylate/ acrylic acid = 33.0/49.5/6.6/10.9

Cyplex 1600 Polyester

Acid Number = 49 0.873 moles/g

% Solids = 74

Molecular Weight: $\bar{M}n$ = 1670 0.599 mmoles/g

$\bar{M}w$ = 4370

1.46 acid groups/mole

Composition:

Isophthalic/phthalic/adipic = 9.3/2.1/4.5 (acid molar ratio)

Neopentylglycol/trimethylolpropane/dipropylene glycol = 72/12/21 (molar ratio of acetates)

TABLE LJM-II

Adsorption of Cyplex 1600 Polyester on R-900(28)
as Measured by SEC

Sample	Ao	Ax	Co (g/l)	Ce (g/l)	Ca (mg/g R-900)
1	20.41	1.327	1.85	0.120	3.77
2	42.29	2.742	3.70	0.240	7.57
3	74.00	5.816	6.66	0.523	13.4
4	102.5	7.098	8.88	0.615	18.1
5	126.4	10.10	11.1	0.886	22.3
6	176.1	13.39	14.8	1.12	29.9
7	255.8	14.50	22.2	1.26	45.8
8	421.1	184.0	37.0	16.2	45.5
9	624.6	364.2	52.2	30.4	47.5
10	919.5	632.8	82.1	56.5	55.9

Ao = Area of initial polyester.

Ax = Area of polyester after adsorption.

Co = Initial concentration of polyester.

Ce = Concentration of polyester in supernatant.

Ca = Concentration of polyester adsorbed on pigment.

TABLE LJM-III

Equilibrium Time for Adsorption of Water-Reducible Vehicles on Several Pigment Surfaces

Pigment	Resin	Surface Type	Time (hrs.)
R-900(28)	Cyplex 1600	Al_2O_3	<1
R-931(01)	Cyplex 1600	Al_2O_3/SiO_2	15
R-960(01)	Cyplex 1600	Al_2O_3/SiO_2	30
SSL-4981	Cyplex 1600	SiO_2	>>100
R-900(28)	XC-4011	Al_2O_3	10
R-931(01)	XC-4011	Al_2O_3/SiO_2	5
R-960(01)	XC-4011	Al_2O_3/SiO_2	5
SSL-4981	XC-4011	SiO_2	>>100

TABLE LJM-IV

Adsorption of Cyplex 1600 on R-900(28)*

Sample	Co (g/l)**	Ce (g/l)**	Ca (g/l)	A (mg/g R-900)
68-1	1.85	0.54	1.31	2.86
68-2	3.70	0.62	3.08	6.73
68-3	6.66	0.84	5.82	12.7
68-6	14.8	1.78	13.0	28.4
68-7	22.2	3.12	19.1	41.7
68-8	37.0	17.4	19.6	42.8
68.9	52.2	32.1	20.1	43.9
68-10	82.1	60.5	21.6	47.2

Co = Initial concentration

Ce = Supernatant concentration

Ca = Concentration of adsorbed polyester

A = Concentration of adsorbed polyester in mg/g of pigment.

*Samples contained 20.6 g. of R-900 and 45.0 ml of polyester solution.

**Measured by UV analysis.

TABLE LJM-V

Adsorption of Cyplex 1600 on R-931(01)

Sample	Co (g/l)	Ce (g/l)	Ca (g/l)	A (mg/g R-931)
150-1	3.53	0.656	2.87	6.27
150-2	5.89	0.778	5.11	11.2
150-3	11.8	1.39	10.4	22.7
150-4	23.6	8.80	14.8	32.3
150-5	29.4	13.3	16.1	35.2
150-6	35.3	18.0	17.3	37.8
150-7	41.2	22.2	19.0	41.5
150-8	58.8	38.3	20.5	44.8
150-9	88.4	67.5	20.9	45.6

TABLE LJM-VI

Adsorption of Cyplex 1600 on R-960(01)

Sample	Co (g/l)	Ce (g/l)	Ca (g/l)	A (mg/g R-960)
114-1	3.29	0.68	2.61	5.70
114-2	5.48	1.35	4.13	9.02
114-3	11.0	4.74	6.26	13.7
114-4	21.9	15.1	6.80	14.8
114-5	27.4	18.5	8.90	19.4
114-6	32.9	21.6	11.3	24.7
114-7	38.4	28.0	10.4	22.7
114-8	54.8	45.2	9.6	21.0

TABLE LJM-VII

Adsorption of XC-4011 on R-900(28)

Sample	Co (g/l)	Ce (g/l)	Ca (g/l)	A (mg/g R-900)
117-1	3.87	0.34	3.53	7.71
117-2	6.45	1.58	4.87	10.6
117-3	12.9	7.54	5.36	11.7
117-4	25.8	19.8	6.00	13.1
117-5	32.2	26.3	5.90	12.9
117-6	38.7	32.1	6.63	14.5
117-7	45.1	38.0	7.07	15.4
117-8	64.5	55.6	8.90	19.4
117-9	96.8	84.3	12.4	27.1
117-10	129.0	117.8	11.2	24.5

Co = Initial Concentration

Ce = Supernatant concentration

Ca = Concentration of adsorbed acrylic

A = Concentration of adsorbed acrylic in mg/g pigment.

TABLE LJM-VIII

Adsorption of XC-4011 on R-931(01)

Sample	Co (g/l)	Ce (g/l)	Ca (g/l)	A (mg/g R-931)
153-1	4.08	1.90	2.18	4.76
153-2	6.80	4.37	2.43	5.31
153-3	13.6	10.7	2.90	6.33
153-4	27.2	24.0	3.20	6.99
153-5	34.0	30.3	3.66	7.99
153-6	40.8	35.7	5.10	11.1
153-7	47.6	42.8	4.80	10.5
153-8	68.0	62.0	6.00	13.5
153-9	102.0	85.5	16.5	36.0

TABLE LJM-IX

Adsorption of XC-4011 on R-960(01)

Sample	Co (g/l)	Ce (g/l)	Ca (g/l)	A (mg/g R-960)
115-1	3.87	3.16	0.71	1.55
115-2	6.45	5.43	1.02	2.23
115-3	12.9	11.5	1.40	3.06
115-4	25.8	24.3	1.50	3.28
115-5	32.2	30.4	1.80	3.93
115-6	38.7	36.9	1.80	3.93
115-7	45.1	40.1	5.00	10.9
115-8	64.5	56.8	7.70	16.8
115-9	96.8	86.6	10.2	22.3
115-10	129.0	106.1	22.9	50.0

TABLE LJM-X

Analytical Characterization of 99.99% TiO_2
(SPEX Ind. Lot No. 10731)

Crystal Structure: 99% rutile

Surface Area: 0.83 m^2/g

Semiquantitative Analysis

	SPEX Industries	CDP Jackson Lab(*)
Fe	30-60 ppm	20 ppm
Si	0.5-2.0 ppm	10 ppm
Al	<1 ppm	20 ppm
Mg		5 ppm
Pb	<1 ppm	5 ppm
Cr	5-20 ppm	1 ppm

(*) It includes matrix correction for TiO_2.

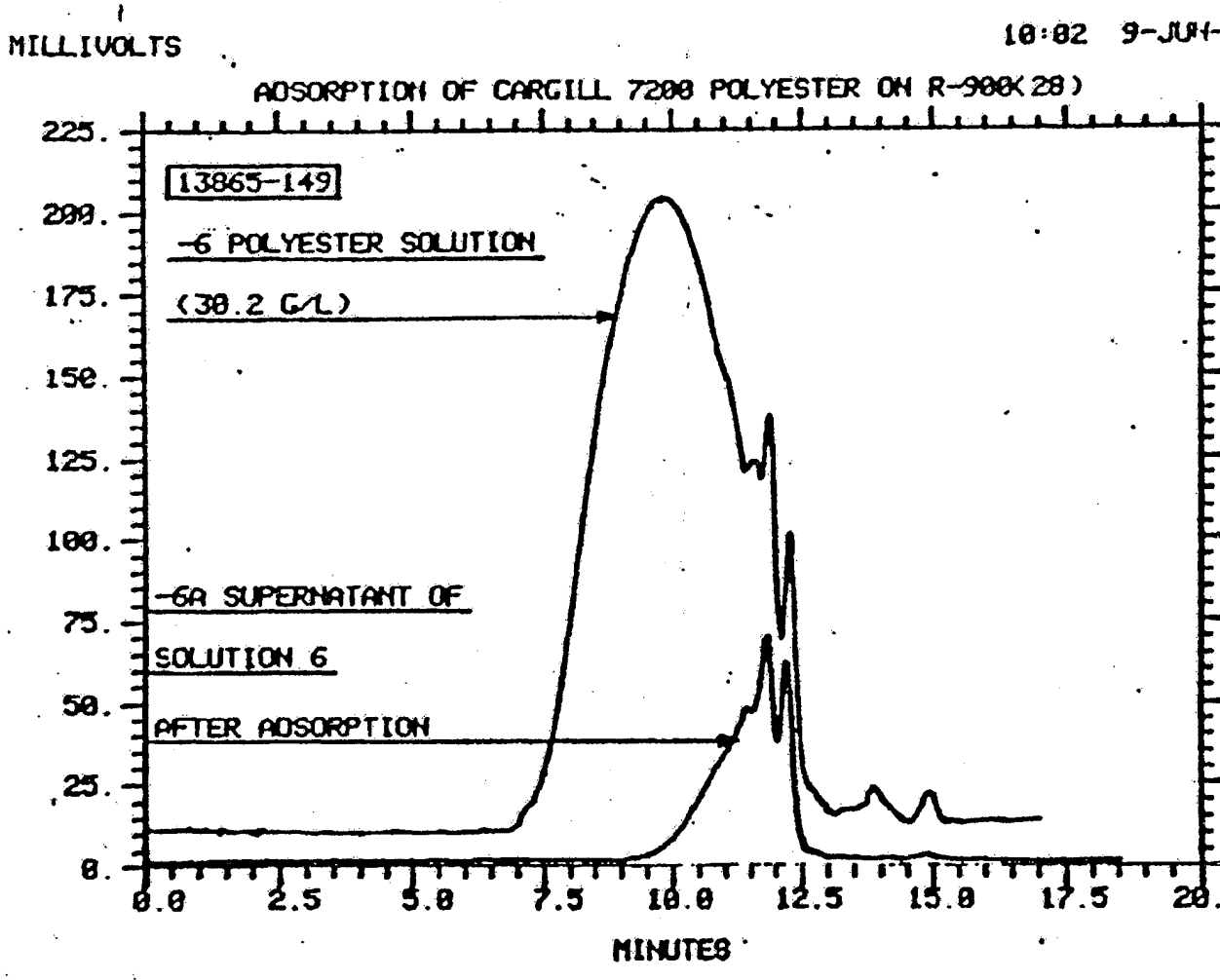


FIGURE LJM-I: ADSORPTION OF POLYESTER RESIN AS DETECTED BY SEC

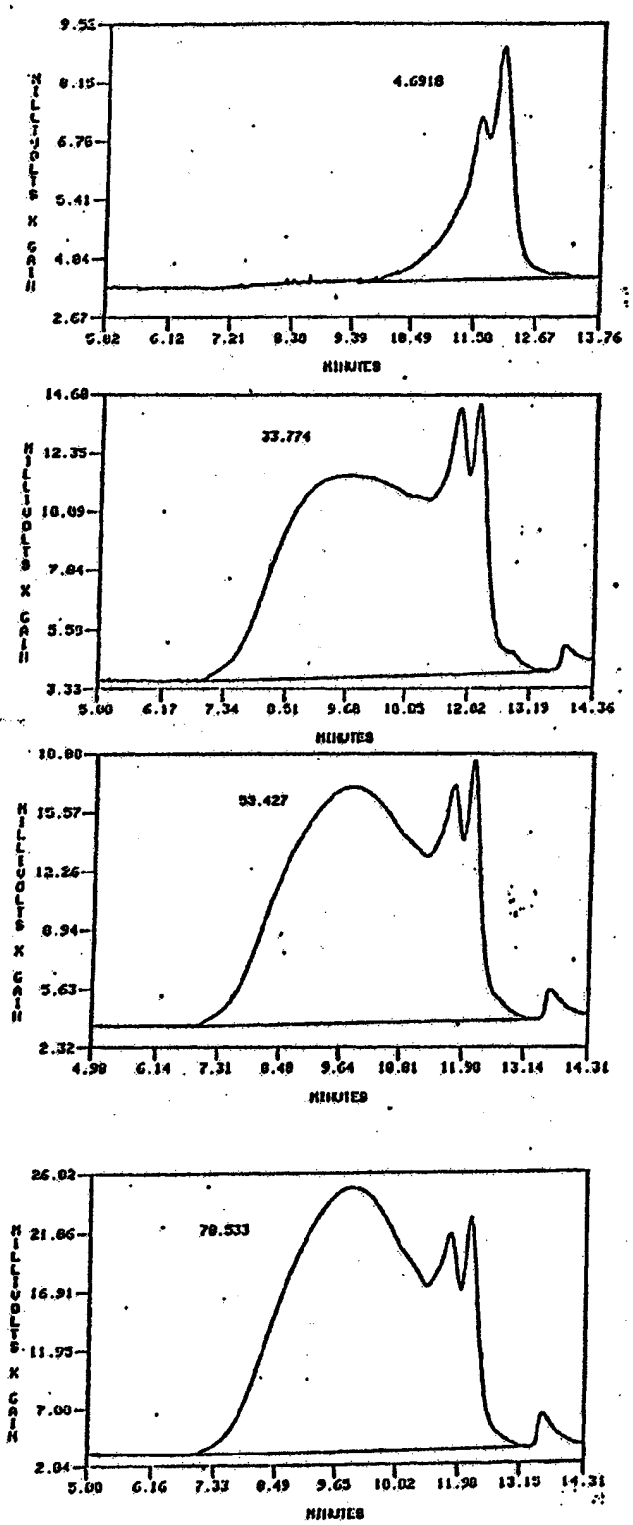


FIGURE LJM-II: MOLECULAR WEIGHT DISTRIBUTIONS ON SUPERNATANT SOLUTIONS OR POLYESTER BEFORE, AT AND AFTER MONOLAYER COVERAGE ON R-900.

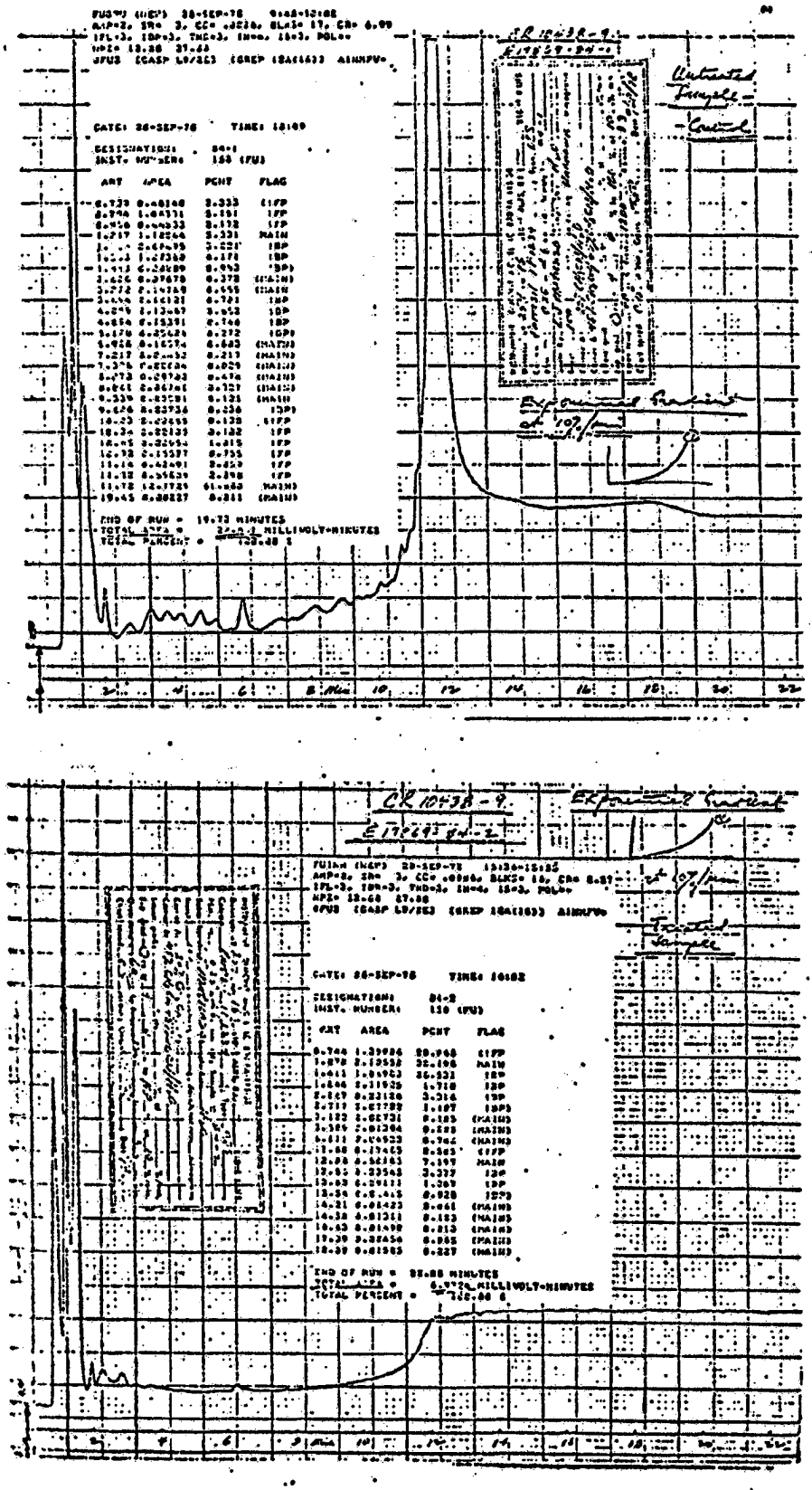


FIGURE LJM-III: REVERSE PHASE CHROMATOGRAMS FOR POLYESTER SOLUTIONS BEFORE (ABOVE) AND AFTER (BELOW) CONTACT WITH R-900. SOLVENT MIXTURE USED A 10% EXPONENTIAL GRADIENT.

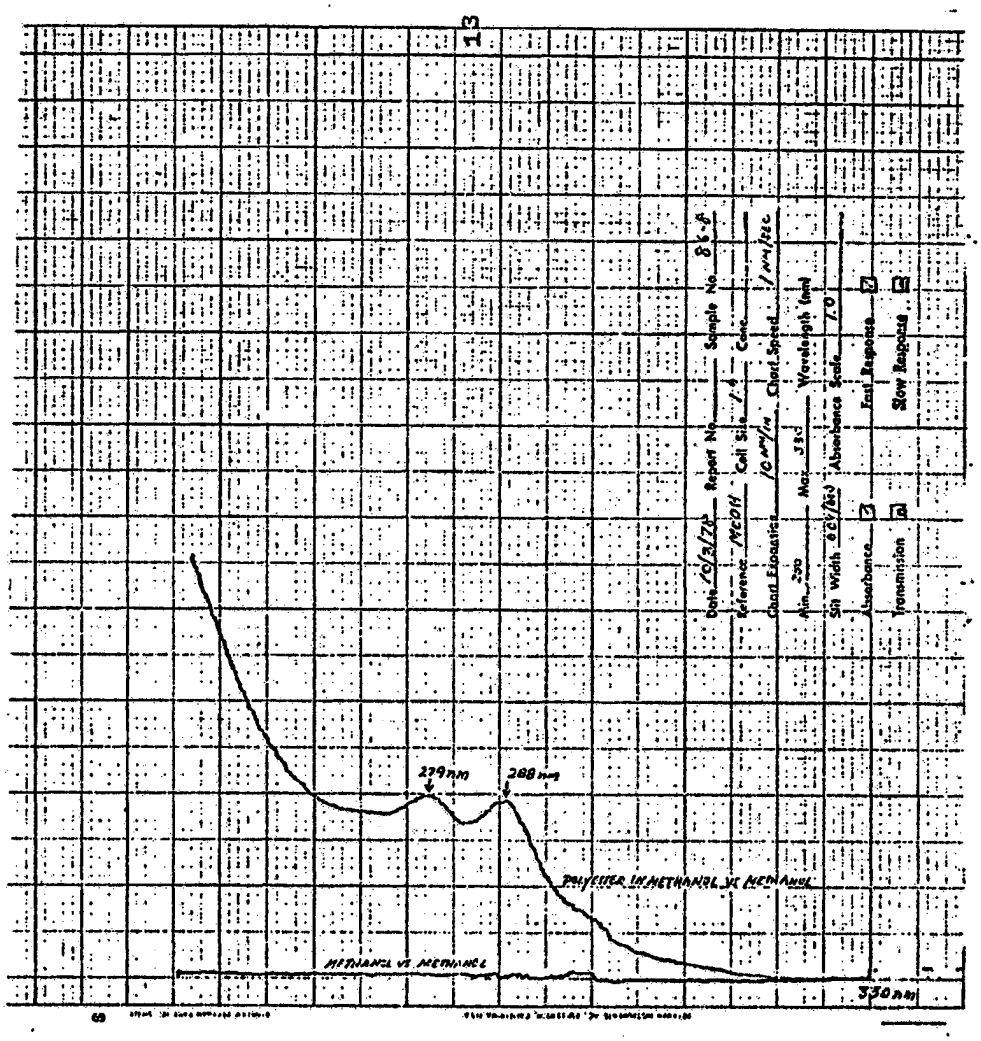


FIGURE LJM-IV: ULTRAVIOLET SPECTRA OF CYPLEX 1600 SOLUTIONS IN METHANOL (ABOVE) AND REFERENCE SOLVENT (BELOW).

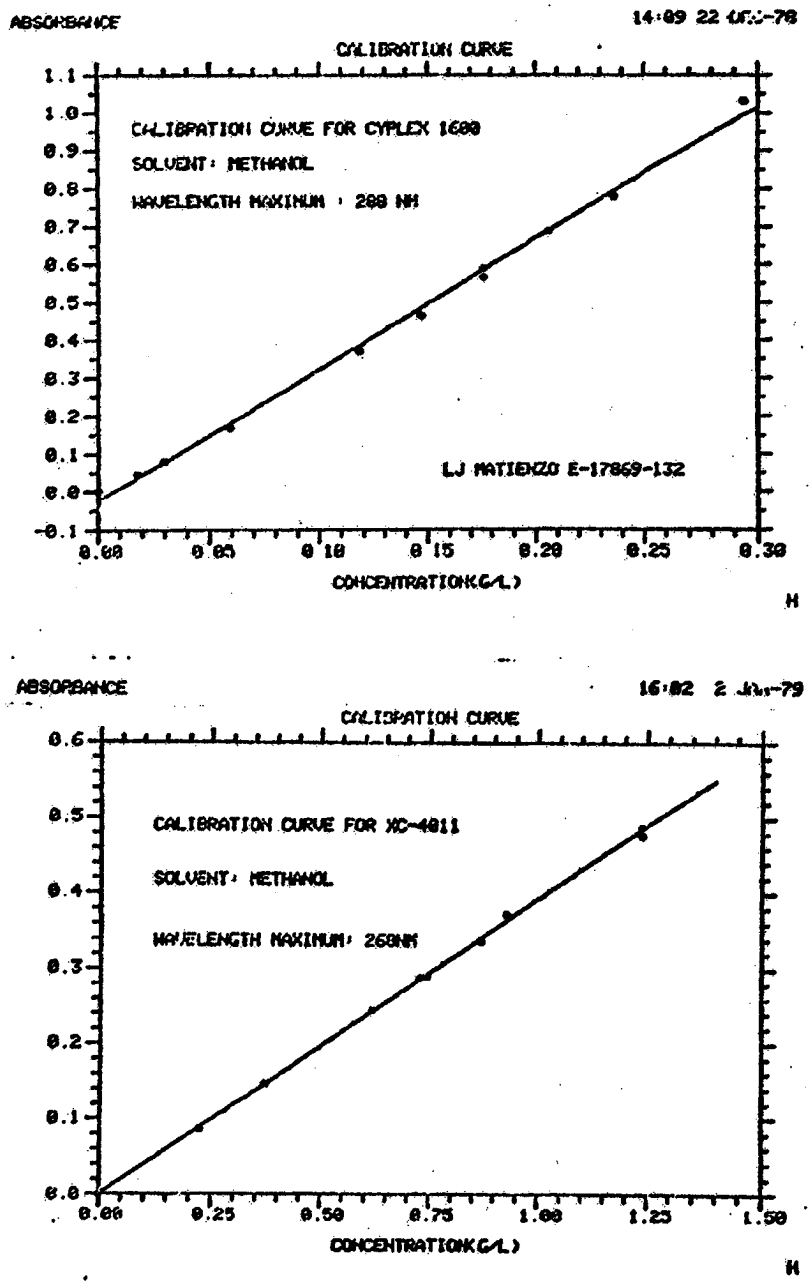


FIGURE LJM-V: TYPICAL CALIBRATION CURVES FOR CYPLEX 1600 (ABOVE) AND XC-4011 (BELOW) METHANOL SOLUTIONS OBTAINED BY ULTRAVIOLET SPECTROSCOPY.

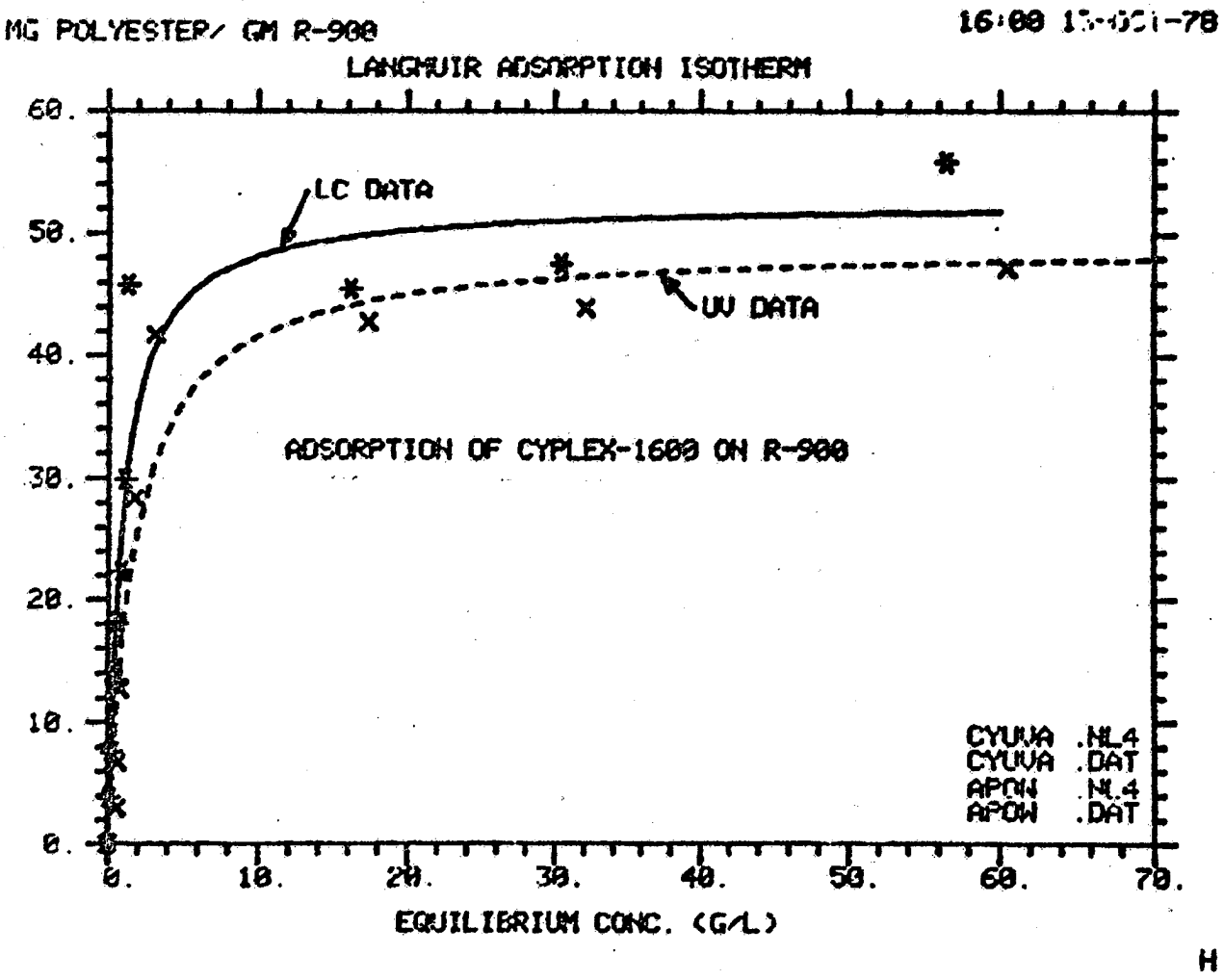


FIGURE LJM-VI: COMPARISON OF ADSORPTION ISOTHERMS OBTAINED BY SEC (LC DATA) AND UV ANALYSIS (UV DATA) FOR THE ADSORPTION OF CYPLEX 1600 ON R-900(28).

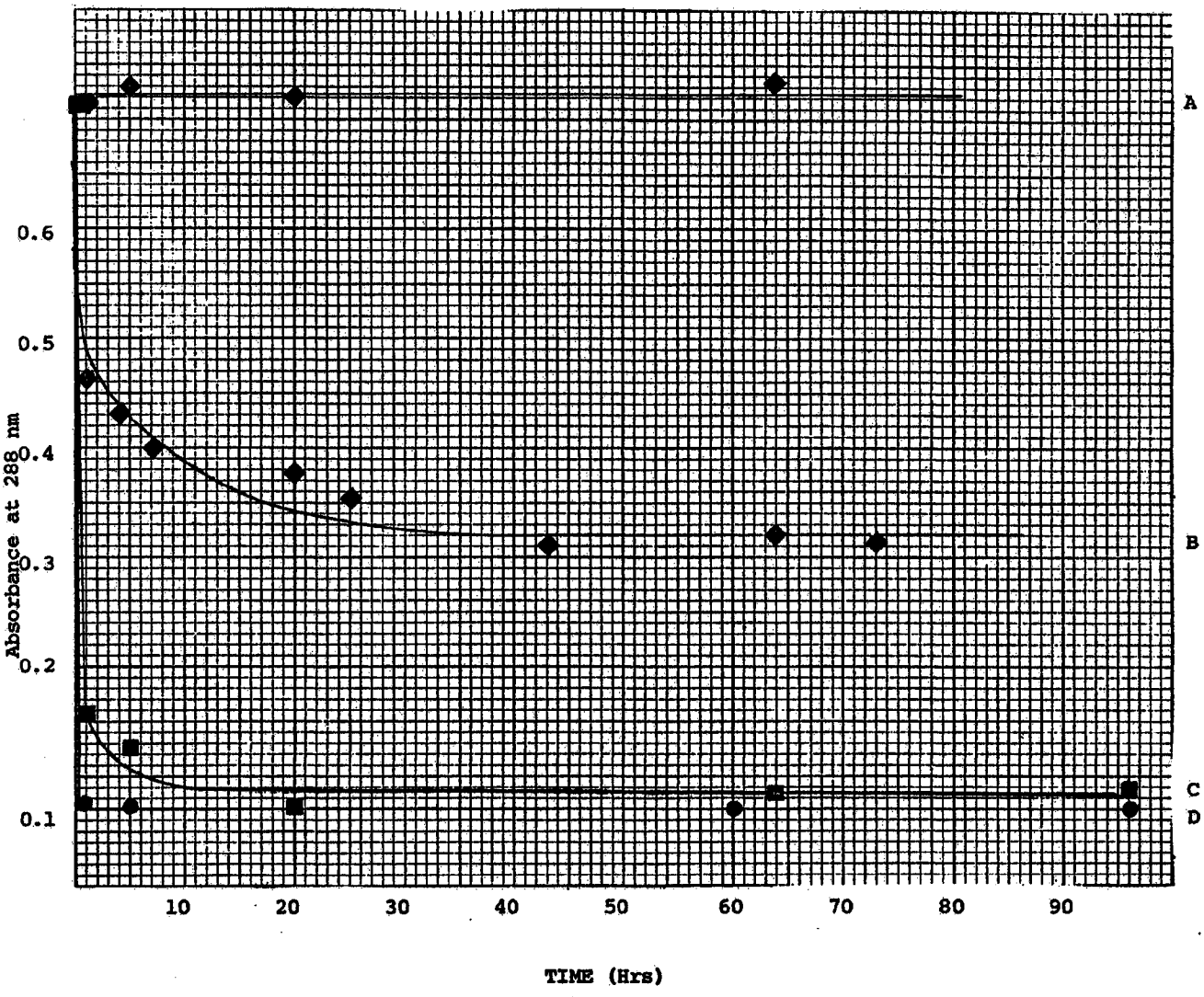


FIGURE LJM-VII: REACTION OF CYPLEX 1600 WATER REDUCIBLE POLYESTER AT SIMILAR INITIAL CONCENTRATIONS WITH:

A) DENSE SILICA COATED PIGMENT (SSL-4981)

B) R-960 (01)

C) R-931 (01)

D) R-900 (28)

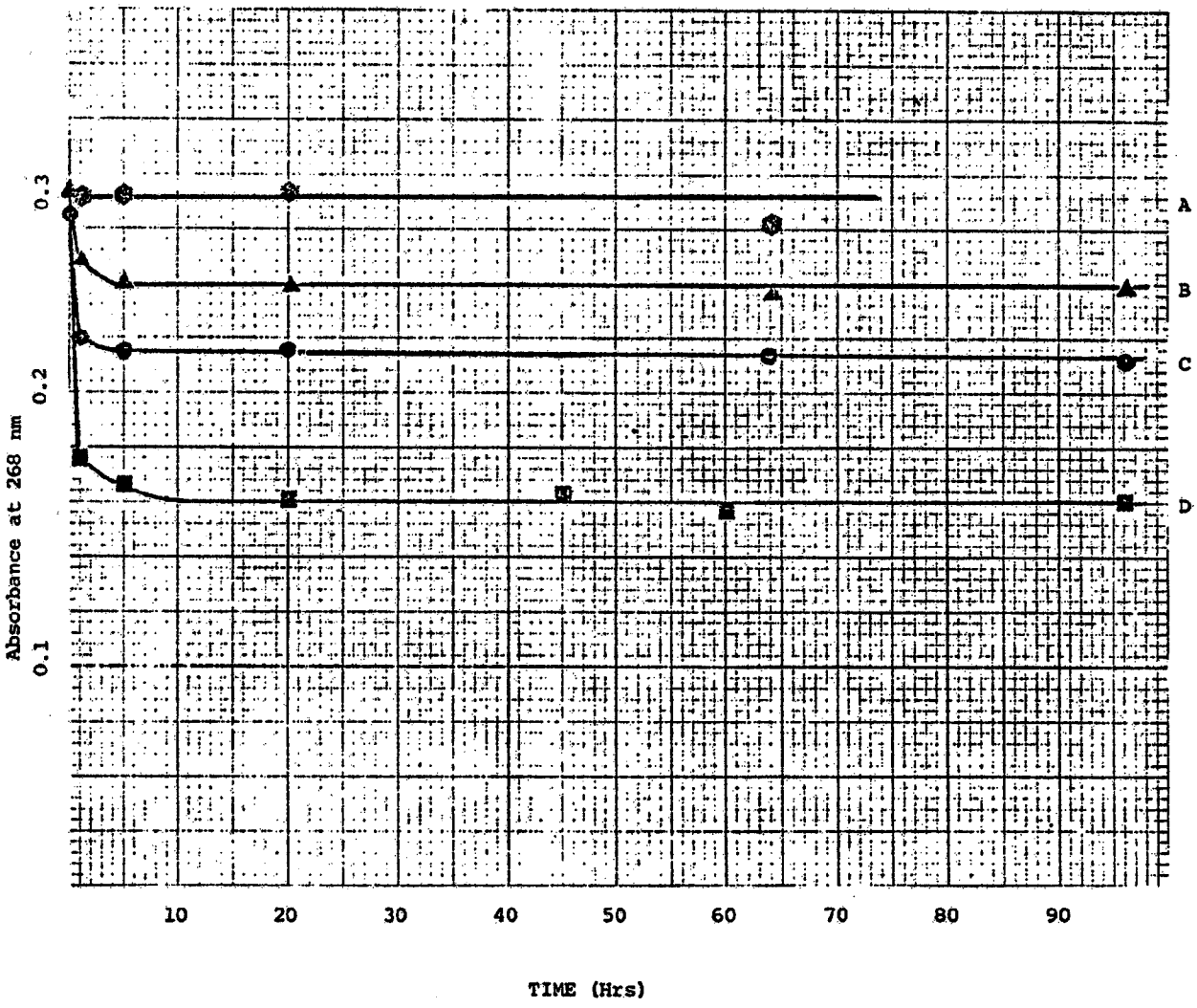


FIGURE LJM-VIII: Reaction of XC-4011 Water Reducible Acrylic At Similar Initial Concentrations With:

A) Dense Silica Coated Pigment (SSL-4981)

B) R-960 (01)

C) R-931 (01)

D) R-900 (28)

ISOTHERMS FOR CYPLEX 1600 POLYESTER ADSORPTION

FROM AQUEOUS SLURRY

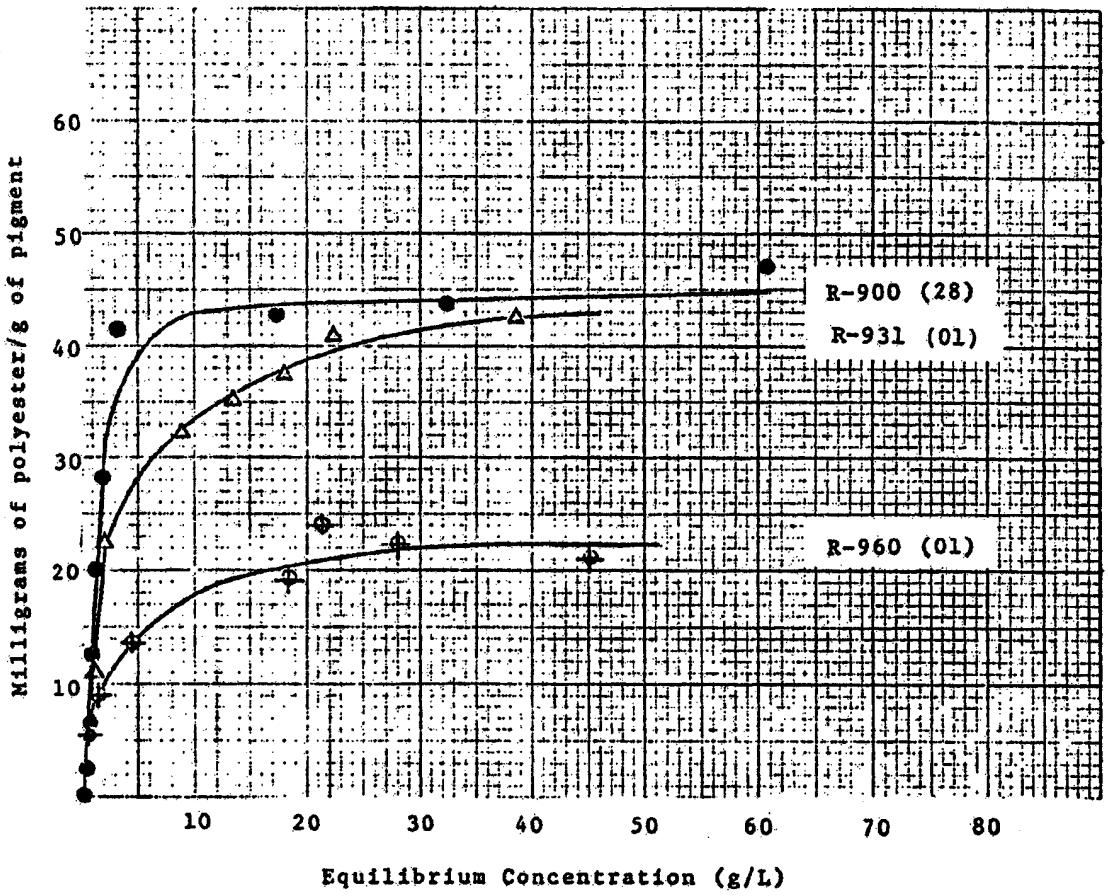


FIGURE LJM-IX: ADSORPTION ISOTHERMS FOR CYPLEX 1600 WITH SEVERAL TYPES OF TI-PURE® PIGMENTS.

ISOTHERMS FOR XC-4011 ACRYLIC ADSORPTION

FROM AQUEOUS SLURRY

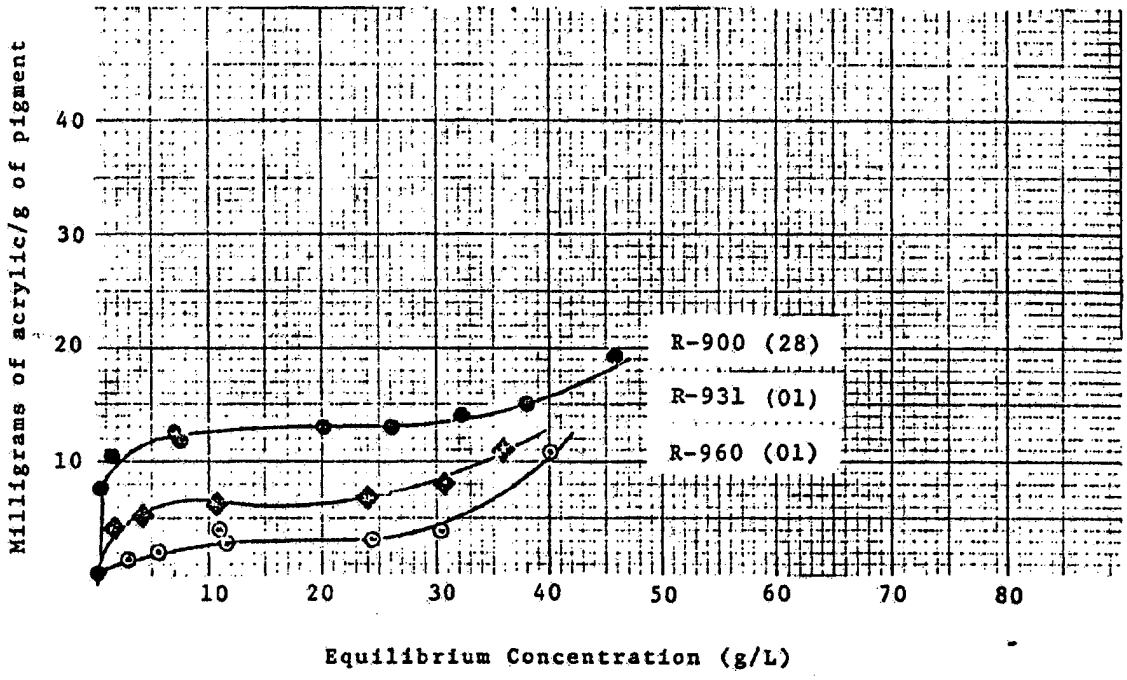
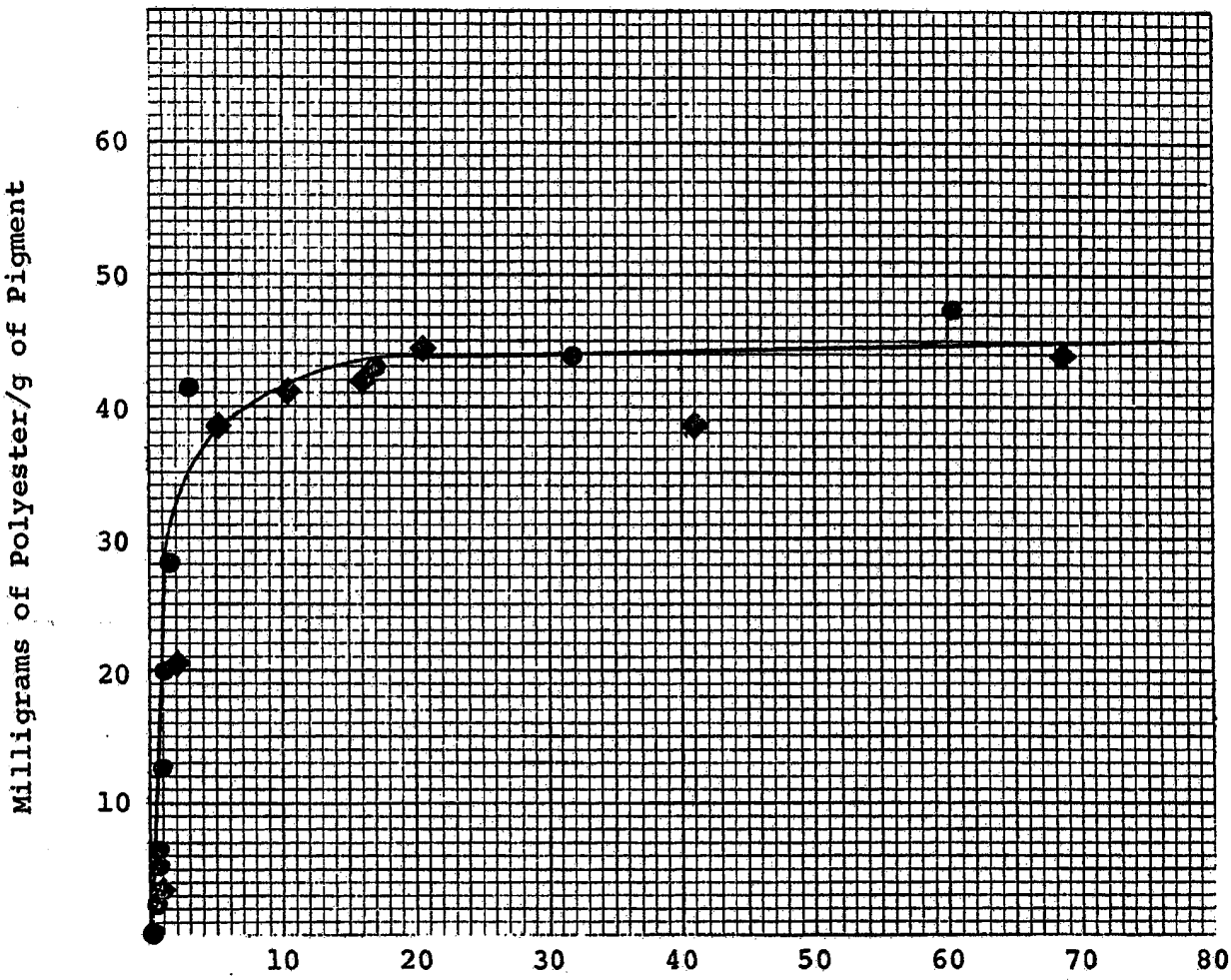


FIGURE LJM-X: ADSORPTION ISOTHERMS FOR XC-4011 WITH SEVERAL TYPES OF TI-PURE® PIGMENTS.

ADSORPTION OF CYPLEX 1600 POLYESTER FROM AQUEOUS SOLUTION ONTO R-900 (28) AND R-900 BASE*



Legend

- ● Data Obtained for R-900 (28)
- ◆ Data obtained for R-900 Base

(*) Material cleaned according to L. Abrams' description.

FIGURE LJM-XI

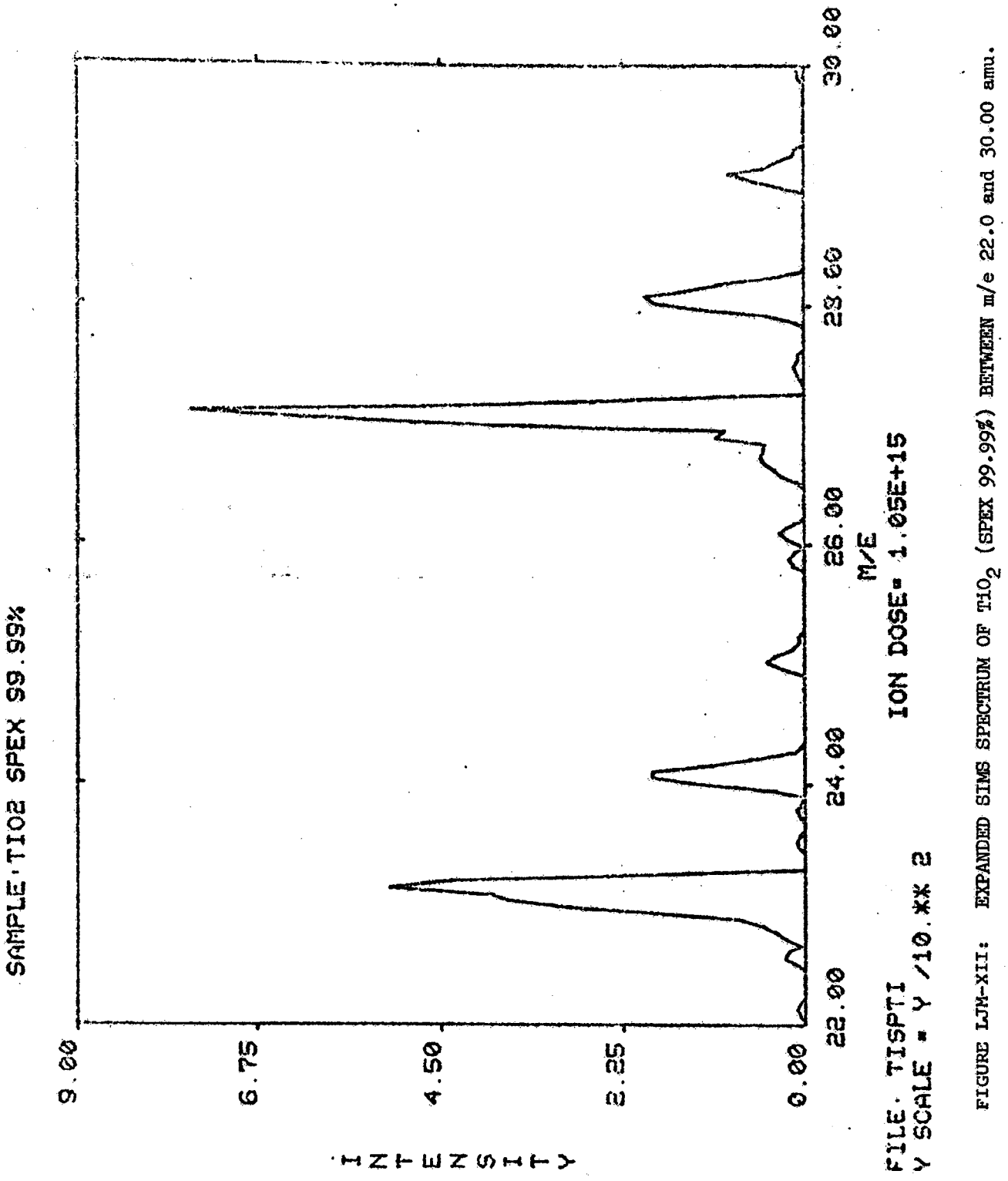


FIGURE LJM-XII: EXPANDED SIMS SPECTRUM OF TiO_2 (SPEX 99.99%) BETWEEN m/e 22.0 and 30.00 amu.

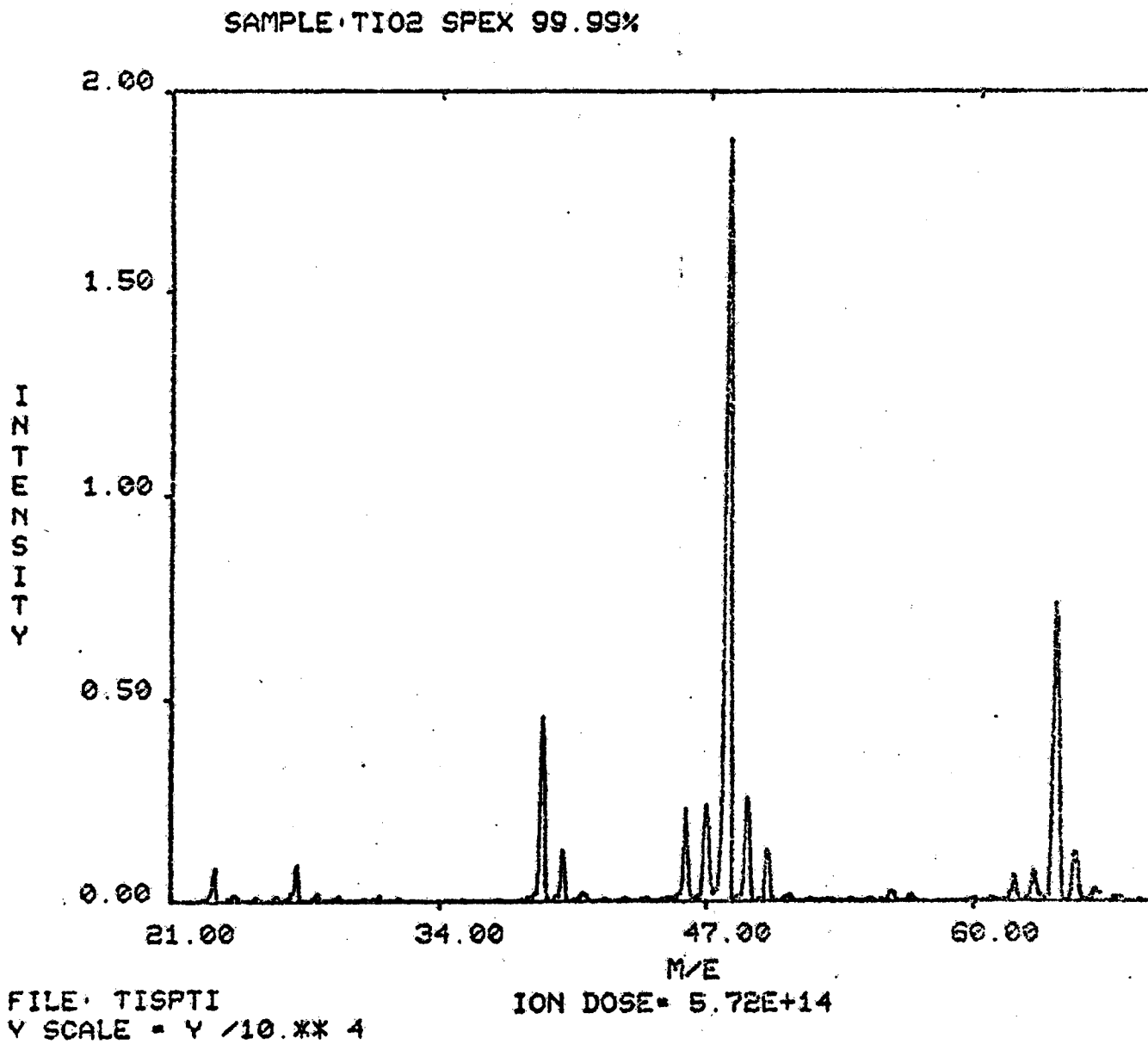


FIGURE LJM-XIII: SIMS SPECTRUM OF TiO_2 (SPEX 99.99%) BETWEEN m/e 21.00 and 73.00 amu.

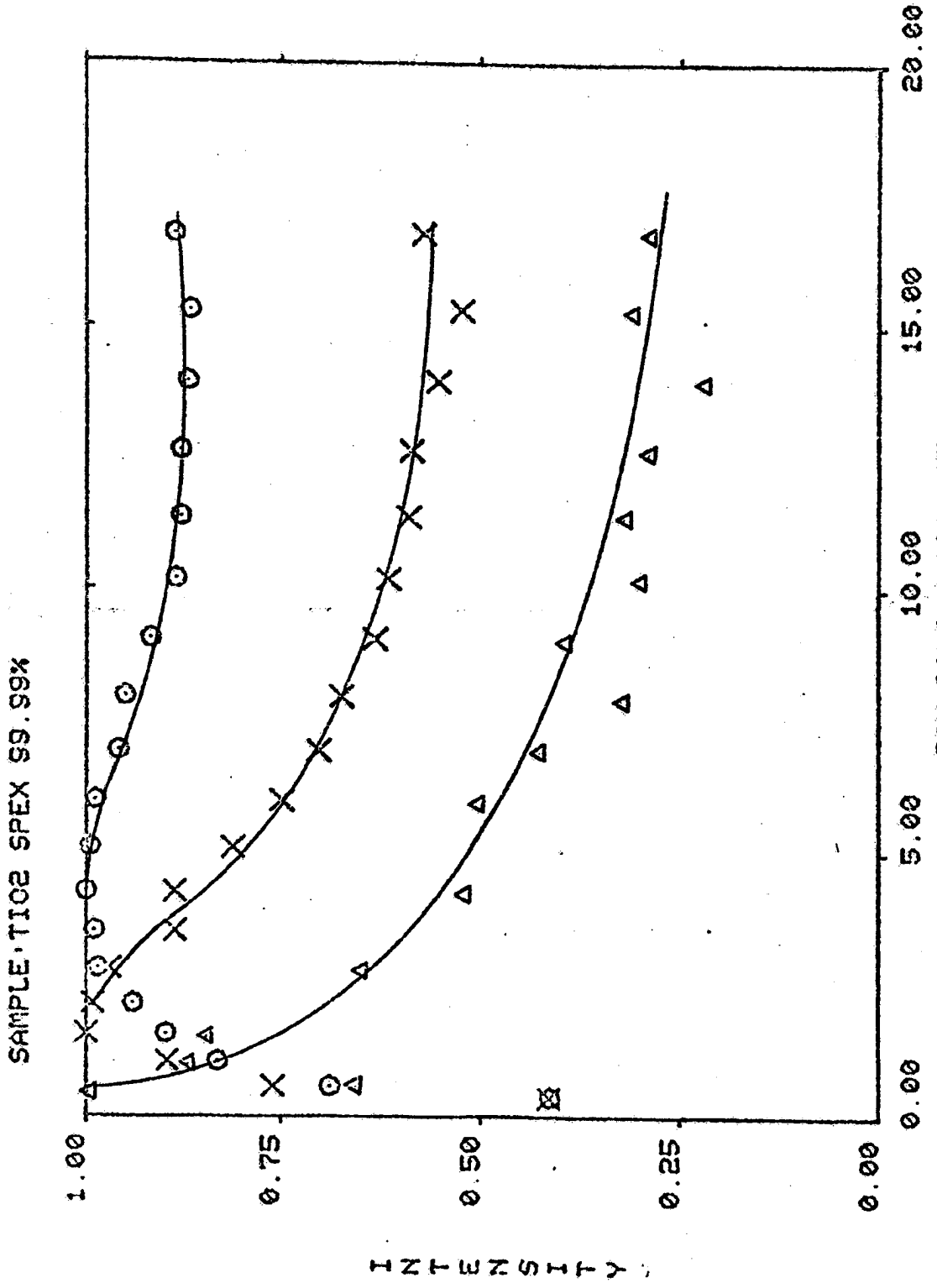


FIGURE LJM-XIV: ETCHING PROFILE OF TiO_2 (SPEX 99.99%) AS DETECTED BY SIMS.

APPENDIX I

PIGMENTS USED IN ADSORPTION STUDIES

Sample	% Al_2O_3	% SiO_2	% TiO_2	Surface Area (m^2/g)
R-900 (28) Lot 4730(*)	3.6	0.1	95.2	12.9
R-960 (01) Lot 6079(*)	2.7	5.8	91.4	12.3
R-931 (01) Lot 6639(*)	N.A.	N.A.	N.A.	14.6
SPEX Ind. TiO_2 99.99%	0.001	<0.002	99.9	0.87
SSL-4981	0.7	1.3	97.8	6.70
CD Base(**)	0.1	0.1	98.2	5.62

(*) Shipping standard

(**) Cleaned Line I NJ Base

N.A.-Not Available

INDEXING TERMS

Acrylic
Adsorption
Alumina
CD Base
Cyplex 1600
Isotherm
Macromolecules
Monolayer
Polyelectrolytes
Polyester
R-900
R-931
R-961
Reverse Phase Liquid Chromatography
Rutile
Silica
SIMS
Sites
Size Exclusion Chromatography
Surface Chemistry
XC-4011
Waterborne

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